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PB80-151566

Characterization of Priority Pollutants from an Airplane Parts Manufacturing Facility

Battelle Columbus Labs, OH

Prepared for

Industrial Environmental Research Lab -Cincinnati, OH

Jan 80

United States
Environmental Protection
Agency

Industrial Environmental Research
Laboratory
Cincinnati OH 45268

EPA-600/2-80-019
January 1980

Research and Development

PB80-151566

EPA

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TECHNICAL REPORT DATA
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1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/2-80-019		PB80-151566

4. TITLE AND SUBTITLE	5. REPORT DATE
Characterization of Priority Pollutants from an Airplane Parts Manufacturing Facility	January 1980 issuing date
	6. PERFORMING ORGANIZATION CODE: G-6617-0601
7. AUTHOR(S): A. K. Reed, M. A. Eischen, M. M. McKown & G. R. Smithson, Jr.	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Battelle's Columbus Laboratories, 505 King Avenue, Columbus, Ohio 43201	10. PROGRAM ELEMENT NO.: A33B1B
	11. CONTRACT/GRANT NO.: 68-03-2552 (T2006)
12. SPONSORING AGENCY NAME AND ADDRESS: Industrial Environmental Research Lab. - Cinn, OH, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268	13. TYPE OF REPORT AND PERIOD COVERED: Final; January-December 1978
	14. SPONSORING AGENCY CODE: EPA/600/12

15. SUPPLEMENTARY NOTES

16. ABSTRACT

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The results of the study show that the treatment practiced at this site removes more than 90 percent of the chromium, zinc and 70 percent of the copper. The system is slightly less effective for cadmium because of its low concentration in the influent to the treatment plant. Nevertheless, in excess of 60 percent of the cadmium is removed. Because of the extremely low concentrations of other metals in the influent to the treatment plant, the effectiveness of the treatment for their removal could not be evaluated with any degree of confidence.

Although the treatment system was not designed for the removal of the priority organic constituents, some are removed during the treatment. This could be due to evaporation or sorption on the solids formed during the precipitation of the metallic components of the wastewater.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution Aircraft Airplane parts manufacturing Wastewater Treatment Lime and settle treatment Sulfur dioxide reduction & neutralization Alkaline chlorination treatment	Pollution control Stationary source	68D

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	41
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

U.S. GOVERNMENT PRINTING OFFICE 1980 -657-146/5547

EPA-600/2-80-019
January 1980

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report contains an assessment of waterborne emissions from a facility in which airplane parts are produced. The study has been conducted to provide a better understanding of the sources, nature, and control of emissions from such facilities. Particular attention has been given to the presence and control of the priority pollutants. Further information on this subject may be obtained from the Metals and Inorganic Chemicals Branch, Industrial Pollution Control Division.

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Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

Wastewater from an airplane parts manufacturing plant was sampled using the U.S. EPA screening protocol for the 129 priority pollutants. The wastewater treatment facilities at this site include batch systems to destroy cyanides, remove oil, and reduce hexavalent chromium to the trivalent state before it is discharged to a system where heavy metals are removed by pH adjustment and settling.

The results of the study show that the treatment practiced at this site removes about 90 percent of the chromium, zinc and 70 percent of the copper. The system is slightly less effective for cadmium because of its low concentration in the influent to the treatment plant. Nevertheless, in excess of 60 percent of the cadmium is removed. Because of the extremely low concentrations of other metals in the influent to the treatment plant, the effectiveness of the treatment for their removal could not be evaluated with any degree of confidence.

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SECTION 1

INTRODUCTION

The Effluent Guidelines Division (EGD), Office of Water Planning and Standards, of the U.S. Environmental Protection Agency (EPA) has been charged with the responsibility for conducting tests to determine the presence of 129 priority pollutants in wastewater from facilities which manufacture nonferrous metals. Specifically, the EPA is obligated to identify toxic priority pollutants and the effectiveness of various treatment processes for removing them from wastewaters generated in the various types of manufacturing facilities, including airplane parts plants. The EGD is required to review the effectiveness of various technologies and to propose and promulgate effluent limitations.

Battelle's Columbus Laboratories (BCL) and Centec Consultants, Inc. undertook the preliminary evaluation of facilities and conducted the sampling and analyses of waste streams at one facility. The data were collected for the Metals and Inorganic Chemicals Branch (MICB), Office of Research and Development, in support of the EGD. The information developed herein is to be used to augment the existing data base. These data also will be used by the MICB to substantiate a metals precipitation manual which is under preparation. Plant operating data are to be used to quantify the performance of the system and to identify factors influencing the characteristics of the samples collected. The activity for this task deals with wastewater discharges from a facility in which airplane parts are fabricated.

This report describes the process, the wastewater treatment facility, and the sampling and analytical protocol, and presents the results and conclusions. The conclusions are based on the sampling program, which showed how effective the wastewater treatment was in removing not only the priority pollutants, but also those tentatively listed as pollutants.

SECTION 2

SUMMARY

A plant site at which airplane parts are fabricated was sampled using EPA screening protocol procedures for the priority pollutants.[1] Before discharging wastewater into a stream, the plant uses an alkaline chlorination treatment to remove cyanides, chemical de-emulsification and settling to remove oil, and sulfur dioxide to reduce hexavalent chromium. (The reduced chromium and other metals are precipitated as hydroxides.) All of the waste streams discharging into the continuous treatment plant were sampled (according to protocol) upstream and downstream of any specific batch treatment used. The influent as well as the effluent of the wastewater treatment plant was sampled during two 7-hour periods of plant operation. The samples were analyzed for the priority pollutants.

The daily waste loads calculated for the metallic priority pollutants and the efficiencies of their removal are shown in Table 1. The other metallic priority pollutants were not detectable.

TABLE 1. EFFICIENCY OF THE REMOVAL OF METALS FROM WASTEWATER PRODUCED IN AN AIRPLANE PARTS FABRICATION PLANT

Priority pollutant	Influent load	Influent concentration	Effluent load	Effluent concentration	Removal efficiency, %
	kg/day	mg/ℓ	kg/day	mg/ℓ	
Cadmium (Cd)	0.055	0.03	0.02	<0.01	63.6
Chromium (Cr)	18.88	10.4	0.436	0.24	97.7
Copper (Cu)	0.27	0.15	0.082	0.045	70.0
Nickel (Ni)	0.055	0.03	0.055	<0.03	--
Zinc (Zn)	0.236	0.13	0.027	0.015	88.6

Based on these results, it is concluded that the treatment as practiced in this facility is very effective in removing zinc and chromium, and slightly less effective for cadmium and copper because of the low concentrations encountered. The effectiveness of this method in removing the other priority metals could not be evaluated with confidence because the low concentrations in the effluent to the treatment plant are probably near solubility limits at pH 8.5.

In general, about 40 percent of the phenol was removed during the treatment of the wastewater in the continuous system. Essentially complete (99.8 percent) removal of the total cyanide was effected in a separate, batch treatment system. There was no appreciable removal of the purgeable halogenated hydrocarbons. Finally, no clear pattern emerged regarding the effectiveness of the treatment for removing other organic priority pollutants. Removal of specific organic components ranged from 0 to more than 99 percent. Although the mechanism of organic removal was not determined, these materials may have been eliminated from the wastewater through evaporation or by sorption on the precipitated metal hydroxides.

SECTION 3

SOURCE DESCRIPTION

PROCESS DESCRIPTION

The plant whose waste treatment facilities were sampled is a parts fabrication and supply center for aircraft assembly plants. Water is used in this plant for sanitary purposes, cooling air compressors and other machinery, rinsing after chemical processing, and preparing coolants for use in machining operations. The cooling water (which is recycle) and the sanitary wastewaters are not included in the scope of the current sampling program. Only the last two categories--the process wastewaters--are included.

The wastewater destined for the process wastewater treatment plant is generated as follows:

- Pickling aluminum, steel and titanium
- Plating chromium, cadmium, nickel, and copper
- Surface conversion coating of chromium on aluminum and phosphate on steel
- Anodizing
- Alodining
- Hot Sealing
- Etching
- Stripping
- Chemical Machining
- Passivating
- Descaling
- Penetrant inspection (Zyglo)^{TM} of aluminum
- Magnaflux of steel
- Mechanical Machining of aluminum and steel
- Heat Treating

The wastewater is treated in the industrial wastewater facility. The facility has sixteen production chemical process tank lines. Ranging in length from six feet to one hundred and fourteen feet. Total tank volume is over 1.3 million gallons of solution with double counter-current flows in all rinse tanks and most rinse tanks contain air agitation. Other innovative procedures include the installation of plastic spheres which float on the surface of process tanks that require elevated temperatures. These spheres conserve heat and chemicals by lowering evaporation rates. Fresh water is supplied by the city, averaging 1.3 million gallons per day. This plant produces around one and one-half million parts per month; principal products

include aircraft skins and wing spars for commercial and military aircraft. Principle raw materials used at the facility are aluminum, steel, titanium, and a wide variety of alloys. Other materials used include:

- o Aliphatic Hydrocarbon Petroleum Solvent
- o Magnaflux ZL60B Penetrent
- o Sherwin D-113A Developer
- o Oakite 60 Descaler
- o Pace SP-112
- o Turco Jet Clean
- o Pennwalt DP1131 - Cutting Compound
- o Oakcut - Drawing Compound
- o Cool Lube 21 (Pacific Chemical Co.) Cutting Compound
- o Pace N-136-B Cutting Compound
- o HO Cut-237 (Houghton) Cutting Compound
- o Velocite 416 (Mobil) Lube Oil
- o DTE-25 Lube Oil
- o CX-305-(Cincinnati Milacron) Cutting Compound
- o CX-305 Cutting Compound
- o Cin Cool C-305 and 202 Lube Oil
- o Grindtex 410 Lube Oil
- o Mobil 45 Lube Oil
- o Mask Coat #2 (Western Coating) - Chemical Mill Maskant
- o 1, 1, 1, - Trichlorethane - Degreaser
- o Various Paints and Common Plating Chemicals

Wastewater Treatment

By far the largest volume of wastewater is produced by chemical processes such as anodizing. Most of the chrome wastewater is generated in the anodizing area from double countercurrent rinse tanks. The chemical processing area generates about 1,515 m^3/day (400,000 gal/day) of wastewater.

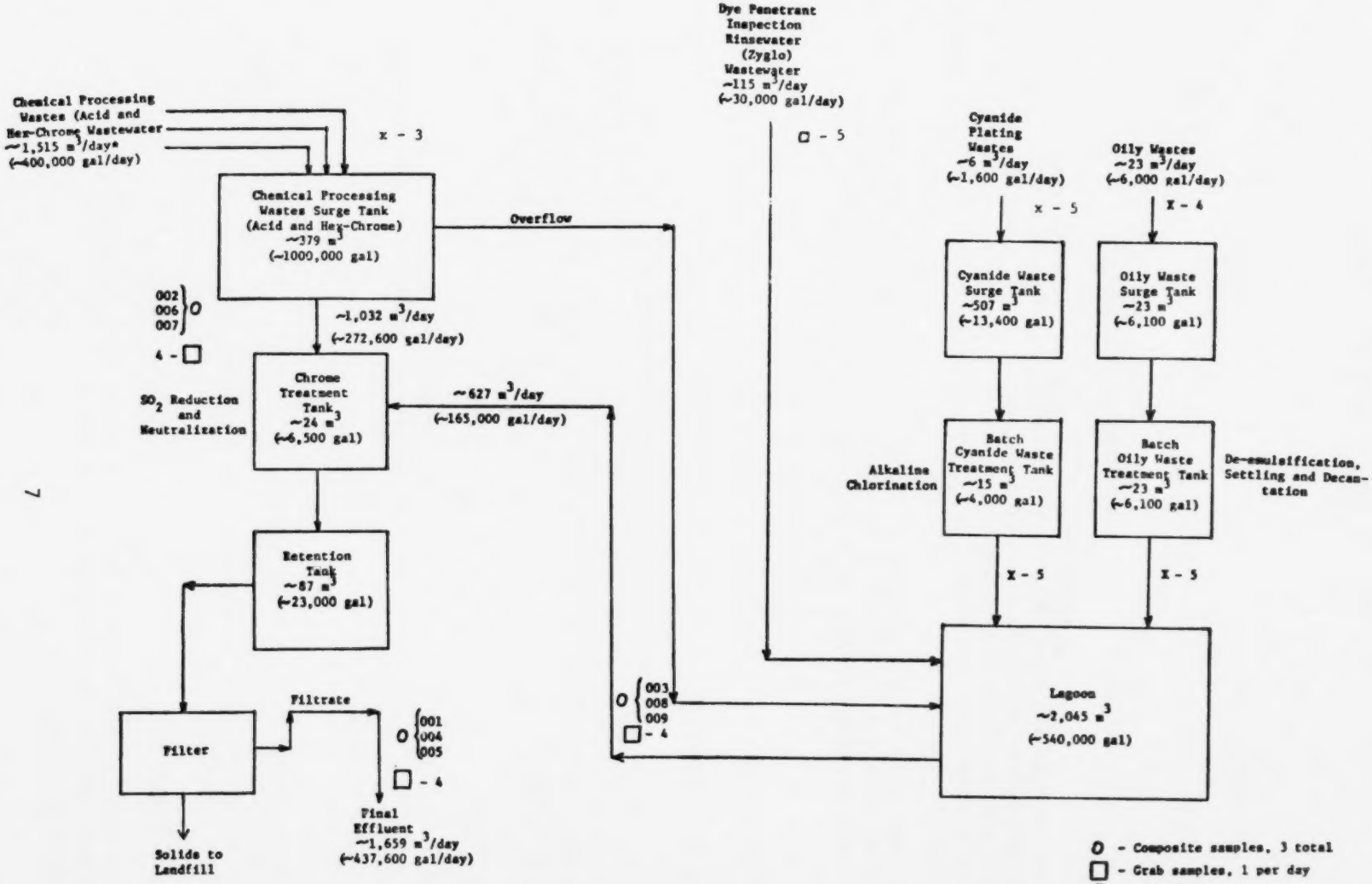
The volumes of wastewaters produced in the other operations are significantly smaller. About 6 m^3/day (1,600 gal/day) of rinsewaters are generated by the electroplating operations in which cyanide baths are used. In addition, about 23 m^3/day (6,000 gal/day) of oily wastes are generated by machining operations, and about 115 m^3/day (30,000 gal/day) of wastewater by nondestructive testing of structural parts (dye penetrant inspection rinsewater--Zyglo).

The relationship of the various manufacturing operations to wastewater loading and treatment are shown in Figure 1. The coding used for identifying the component samples also is shown in Figure 1. As shown there, both the cyanide wastes and the oily wastes are treated in batches prior to being discharged into a lagoon.

Approximately two batches of cyanide wastewater are treated each week, using conventional alkaline chlorination to detoxify the wastewater by destroying the cyanide. In addition, two batches of oily wastewater are treated each day, using chemical de-emulsification, settling, and decantation to remove the oil and other pollutants.

The Zyglo rinsewater and the chrome surge tank overflow flow intermittently into the spills lagoon. Wastewater from both the chrome surge tank and the spills lagoon is pumped into the continuous treatment system where the hexavalent chromium is reduced to the trivalent state with sulfur dioxide. Excess sulfur dioxide (10 mg/) is used to ensure complete reduction of the hexavalent chromium. The metallic components are precipitated as hydroxides by adjusting the pH of the wastewater with lime.

The underflow from the clarifier is centrifugally dewatered to remove the solids and the solid residue is transported to a landfill. The clarified effluent flows through a storm sewer which discharges into Stuck Creek.


Chemical Processing Wastes (Acid and Hex-Chrome Wastewater ~1,515 m³/day* (~400,000 gal/day)
x - 3
Chemical Processing Wastes Surge Tank (Acid and Hex-Chrome) ~379 m³ (~1000,000 gal)
Overflow
002 006 007 O
~1,032 m³/day (~272,600 gal/day)
4 - □
SO2 Reduction and Neutralization
Chrome Treatment Tank ~24 m³ (~6,500 gal)
~627 m³/day (~165,000 gal/day)
Retention Tank ~87 m³ (~23,000 gal)
Filter
Filtrate
001 004 005 O
□ - 4
Solids to Landfill
Final Effluent ~1,659 m³/day (~437,600 gal/day)
Dye Penetrant Inspection Rinsewater (Zyglo) Wastewater ~115 m³/day (~30,000 gal/day)
□ - 5
003 008 009 O
□ - 4
Cyanide Plating Wastes ~6 m³/day (~1,600 gal/day)
x - 5
Oily Wastes ~23 m³/day (~6,000 gal/day)
X - 4
Cyanide Waste Surge Tank ~507 m³ (~13,400 gal)
Oily Waste Surge Tank ~23 m³ (~6,100 gal)
Alkaline Chlorination
Batch Cyanide Waste Treatment Tank ~15 m³ (~4,000 gal)
Batch Oily Waste Treatment Tank ~23 m³ (~6,100 gal)
De-emulsification, Settling and Decantation
X - 5
X - 5
Lagoon ~2,045 m³ (~540,000 gal)
O - Composite samples, 3 total
□ - Grab samples, 1 per day
X - Grab samples, once only

*Flows shown are nominal flows.

FIGURE 1. Diagram of water flow, airplane parts fabrication plant, showing sampling locations.

SECTION 4

SAMPLING AND ANALYTICAL APPROACH FOR SCREENING TESTING OF PRIORITY POLLUTANTS

To determine the presence or absence of priority pollutants in wastewater discharges from an airplane parts fabrication plant, the approach described in this section was developed for sampling, analysis, and screening testing. Because of the separate pretreatment of portions of the waste stream, waste streams were sampled at two stages--not only as commingled effluent, but also before commingling.

The precautions taken to meet stringent quality assurance guidelines in the sampling procedure, field flow measurements, and analytical procedures (i.e., sampling and analytical protocol) are described in this section of the report.

SAMPLING PROCEDURES

Presampling Preparation

All presampling activity was directed at assembling, cleaning, and storing sample containers to be used in the field according to the procedures outlined in "Appendix III, Collection of Samples for Screening Analysis," in Sampling and Analysis Procedures for Screening Industrial Effluents for Priority Pollutants.[1] Sample containers were cleaned, rinsed with organic-free water, drained, and air- or oven-dried at 100°C as appropriate.

Sampling Sites

During an initial survey of the plant, sampling sites were chosen. Sampling points were located at the influent to the treatment plant (between the chrome surge tank and the continuous treatment system and between the lagoon and the continuous treatment system). The effluent being discharged from the continuous treatment system also was sampled. Upstream sampling points of the wastewater from the industrial operations are noted in Figure 1. The sampling sites and the coding used in the field to identify the samples and record information on the progress of the sampling in a permanent record book* are shown in Figure 1. Organic-free distilled water supplied by BCL was used as a blank.

Collection Techniques

Three areas assumed to be critical in the overall wastewater collection and treatment facility were sampled as composites:

*BCL Log Book No. 33888

- The influents to the treatment plant (002 and 003; 006 and 007) were composited manually over two 7-hour periods. The manual collection took place every 2 hours using a 600-mℓ beaker filled to 300 mℓ. All composites were collected in 10,000-mℓ bottles (glass) and kept at ice temperature.

- Two 10,000-mℓ composites of treatment plant effluent (001 and 004) were collected manually in the same two 7-hour periods using the same technique described above. Again, all samples were kept iced during and after the sampling period.

- Duplicate composites of both influents and the continuous treatment plant effluent also were collected manually during the second 7-hour period.

A continuous sampling unit was not used because of delays by the airline during the shipment of the equipment.

Grab samples for phenols, cyanide, metals, and organics were taken once. These samples were taken before and after the continuous treatment system as well as before and after each of the pretreatment units.

- Each sample for cyanide analysis was collected in a 1-liter amber polyethylene bottle and preserved with 0.6 gram of ascorbic acid and at least 2 mℓ of 10N NaOH; final pH = 10.0.

- Each sample for phenol was collected in a 1-liter glass bottle and preserved with 2 mℓ H_2SO_4 (conc.), if pH was greater than 4.

- Samples for benzene (volatile organics) were collected in 8-oz glass bottles with extra precautions taken during filling to eliminate entrapped air bubbles at the Teflon/silicone septa cap.

- Samples for metals were collected in 8-oz glass bottles. Preservatives were not added.

- Each set of grab samples had its own blank of organic-free distilled water sample prepared.

All sampling events were recorded in a permanent record book and specially prepared labels were marked with waterproof markers and affixed with waterproof tape. A log of the grab samples and composites was prepared and is appended to this report.

Sample Shipping

The collected samples were kept at ice temperature while being transported from the plant site to BCL by air. Once at BCL, the samples were stored in a cooler set at 4°C until they were split.

Sample Splitting

The composited samples were split according to the recommendations cited in the "Collections of Samples for Screening Analyses of Priority Pollutants;"[1] that is, by syphoning into five clean bottles after magnetic stirring of the composite using a Teflon stirring bar. Polyethylene tubing equipped with a Viton rubber tip was used to make the transfers. The system was washed thoroughly and rinsed with organic-free distilled water between uses. The bottles were cleaned using 1N HNO_3 and at least triple rinsed with "blank" water (Milli-Q-Water), drained, heated to 200°C, and cooled to room temperature in a dust-free area. Caps also were cleaned and lined with close-fitting Teflon liners. The bottles were labeled and coded in sets of five (one 16-oz bottle and four 32-oz bottles), to match the composite being split. The five samples were to be used for the following purposes and were identified as such:

- Metals (MET)
- Pesticides, PCB, and asbestos (P&P)
- Gas chromatography/mass spectroscopy (GC/MS)
- Classic parameters (CP)
- Company's sample.

The remainder of the composite was stored at 4°C for further use if needed.

The coding used to identify the split samples matched that used to identify the streams sampled in the field (i.e., 000 through 009).

All of the samples split from the composite were stored at 4°C until their submission for analysis. Custody of these samples was transferred formally to the analytical team with a list of their identity, origin, and analyses required.

FLOW MEASUREMENT

The flow rate of the effluent from the treatment plant is metered. The influent from the holding tank and from the lagoon are pumped to the treatment plant. Flows from these sources were estimated on the basis of the flow control valve settings and the duration of the pumping periods. On the basis of the material effluent, the volumes for the sampling period waste load calculations are based on 1,815 m^3/day (480,000 gal/day).* The materials from the Zyglo holding tank, the cyanide batch treatment system, and the oily waste treatment materials were discharged in batches into the lagoons. Their daily volumes were estimated on the basis of the levels of liquids in the respective tanks. The total influent from the chromium holding tank and from the lagoon to the treatment plant consisted of ~1,190 m^3/day (315,000 gal/day) and ~625 m^3/day (165,000 gal/day), respectively.

* The flows during the sampling period were slightly different from the nominal flows shown in Figure 1, e.g., a total effluent of 1,815 m^3 vs 1,659 m^3.

ANALYTICAL PROCEDURES AND QUALITY ASSURANCE

The analytical procedures and quality assurance methodologies were those set forth in the U.S. EPA screening protocol[1] except where specifically noted. The analytical results are summarized in each of the sections related to specific elements or compounds. The sample numbers in the tables of analytical data are the base numbers recorded in Battelle Report Book No. 33888 (see section on sample splitting). Quality assurance information is given in the sections relevant to these materials.

Metals

Samples for all metal determinations with the exception of mercury were concentrated by acidifying 200 mℓ with nitric acid and evaporating to 50 mℓ. Perkin-Elmer Models 305B and 603 atomic absorption spectrophotometers were used for the metal analysis. The conventional air-acetylene flame method was used for the determination of Ag, Cd, Pb, Cu, Zn, Cr, and Ni, while Be was determined using a nitrous oxide-acetylene flame. The HGA Graphite Furnace technique was used for determining Sb and Tl. Analyses for Se and As were carried out using the hydride generation-flame method in which the metal is converted to a volatile hydride and introduced into a hydrogen-nitrogen air entrained flame. Mercury was determined on an aliquot of the original samples by a cold vapor technique in which the mercury is reduced, amalgamated onto silver wool, and then released into an absorption cell by heating the silver wool.

Results of the atomic absorption analyses are given in Table 2.

To provide quality assurance, measured amounts of the elements being determined were added to the blank, which was acidified for further confirmation of the accuracy of the procedures. The spike and recovery data are presented in Table 3. Not enough sample was available for duplicate analyses.

Total Cyanides

The influents to and effluents from the continuous treatment plant were analyzed for total cyanide using the procedures set forth in the U.S. EPA screening protocol[1]. The results of these analyses are given in Table 2. In addition, samples of the influent to and effluent from the batch cyanide treatment system for 6/22/78 were analyzed for total cyanides. The results of these analyses also are given in Table 2.

Quality assurance for the total cyanide analysis was provided by analyzing two standard samples as well as a spiked sample of the influent to the continuous treatment plant. Further quality assurance was provided by analyzing these samples both colorimetrically and volumetrically. The quality assurance data are presented in Table 4.

Organic Constituents

The general procedure used for the determination of the priority organic pollutants is outlined in Figure 2. The compounds which were sought included

TABLE 2. RESULTS OF ATOMIC ADSORPTION AND TOTAL CYANIDE ANALYSES (mg/ℓ)[a]

Sample no.[b]	Se	As	Hg	Sb	Be	Tl	Ag	Cd	Pb	Cu	Zn	Cr	Ni	CN[c]
001	<.001	.0006	<.0002	<.005	<.005	<.003	<.01	<.01	<.05	0.05	.01	.28	<.03	.05[d]
002	<.001	.001	<.0002	<.005	<.005	<.003	<.01	<.01	<.05	0.13	.12	12	<.03	
003	<.001	.0009	<.0002	<.005	<.005	<.003	<.01	.03	<.05	0.18	.15	8.9	.03	.05[d]
004	<.001	.0004	<.0002	<.005	<.005	<.003	<.01	<.01	<.05	0.04	.02	.20	<.03	
004-005														.05[e]
006	<.001	.001	<.0002	<.005	<.005	<.003	<.01	.07	<.05	0.16	.14	11	.03	
008	<.001	.0006	<.0002	<.005	<.005	<.003	<.01	.02	<.05	0.14	.12	7.8	.03	
008-009														0.15[e]
032														22.0[e]
037														.05[e]

(a) Analyses were completed July 7, 1978.

(b) Sample No. — Sample site

- 001 — Treatment plant effluent [d]
- 002 — Treatment plant effluent [d]
- 003 — Influent from lagoon [d] from wood tank
- 004-005 — Treatment plant effluent [e]
- 006 — Treatment plant influent from wood tank [e]
- 007 — Treatment plant influent from wood tank [e]
- 008-009 — Treatment plant influent from lagoon [e]
- 032 — Influent to cyanide treatment [e]
- 037 — Effluent from cyanide treatment [e]

See page 26-27 for complete sample listing

TABLE 3. QUALITY ASSURANCE FOR METAL ANALYSES

Sample	Element	Spike recovery data			
		Amount present, mg	Amount added, mg	Amount found, mg	Percent recovery
Acid blank	Se	<0.001	10.0	10.3	103
Acid blank	As	<0.0001	10.0	9.4	94
Reagents blank	Hg	0.016	0.100	0.117	101
Acid blank	Sb	<0.005	10.0	9.5	95
Acid blank	Be	<0.005	10.0	10.0	100
Acid blank	Tl	<0.003	10.0	9.0	90
Acid blank	Ag	<0.01	10.0	9.4	94
Acid blank	Cd	<0.01	10.0	10.0	100
Acid blank	Pb	<0.05	10.0	10.0	100
Acid blank	Cu	<0.01	10.0	9.5	95
Acid blank	Zn	2.5	10.0	10.0	80[a]
Acid blank	Cr	6.5	10.0	16.5	100
Acid blank	Ni	2.8	10.0	12.5	98

(a) Discrepancy in recovery in excess of the ± 15 percent permitted by the protocol[1].

TABLE 4. QUALITY ASSURANCE DATA FOR TOTAL CYANIDE ANALYSES

Sample	CN^- present, mg	CN^- added, mg	CN^- found, mg		Percent recovery	
			Colorimetric	Volumetric	Colorimetric	Volumetric
Standard	<0.05	1.281	1.230	1.273	96.0	99.4
003[a]	<0.05	0.128	0.111	0.127	86.7	99.2
Standard	<0.05	0.640	0.640	0.658	100	102.8

(a) Influent from lagoon to treatment plant (6/21/78).

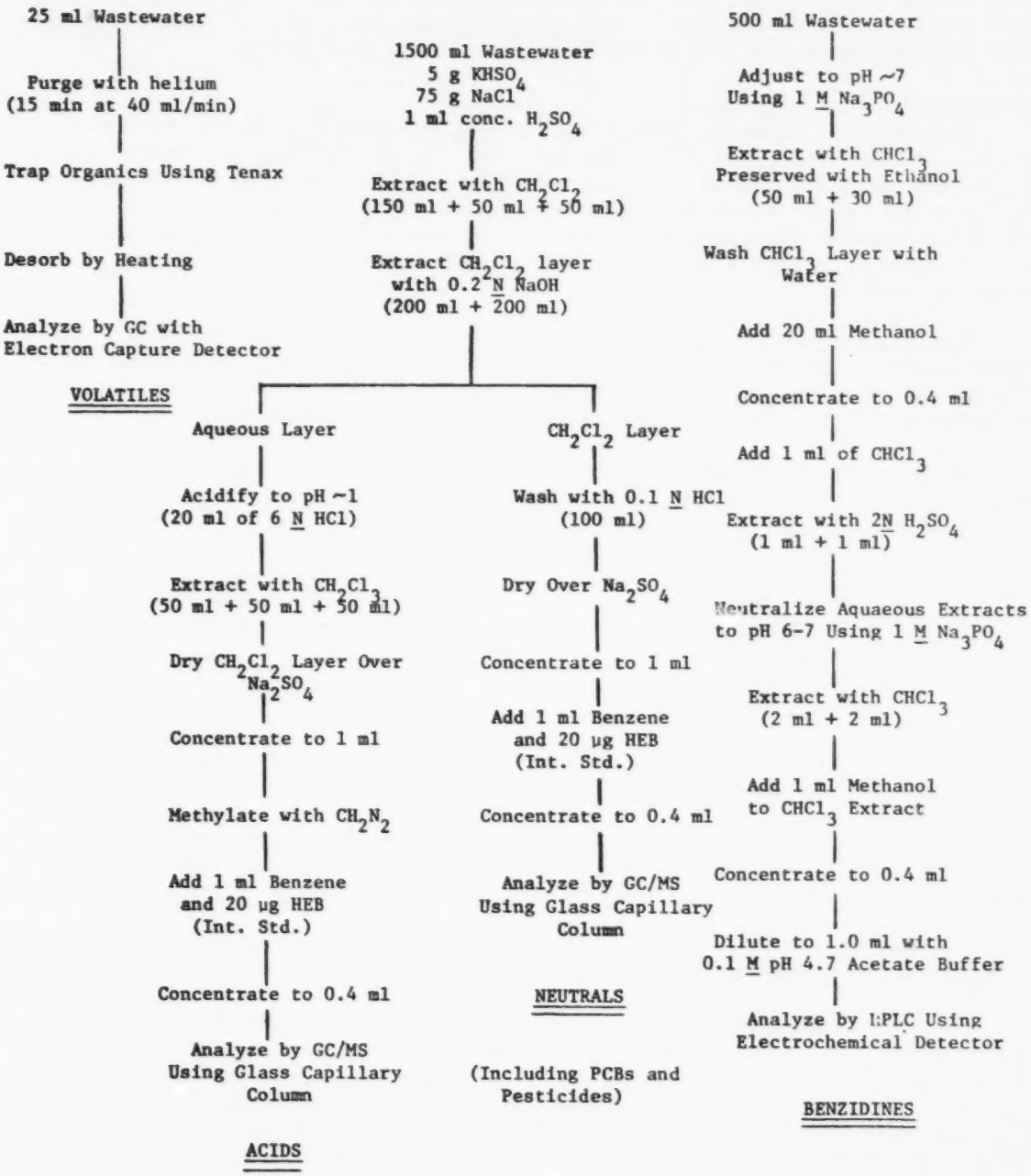


Figure 2. Scheme for Analysis of Wastewater.

volatile organic compounds, base-neutral extractables, phenolic compounds, and benzidines. In general, the U.S. EPA screening protocol[1] in effect at that time was followed during the performance of these analyses. A summary of the specific procedures which were used is included as Appendix B.

Volatile Organic Compounds--

Battelle was asked to analyze six composite samples from the Boeing, Seattle, Washington plant for organics. The "Purge and Trap Gas Chromatography" method was used for determining the volatile organic compounds. This method includes the use of a Tekmar liquid sample concentrator (LSC-1) to concentrate the water samples and a Packard, Series 800, gas chromatography instrument with an electron capture detector for analysis. The results obtained are shown in Table 5.

The most volatile compounds, such as vinyl chloride, chloroethane, and methylene chloride were not detected; therefore, if present, they would be at a level of less than 0.01 µg per liter. The compounds reported appear to be the compounds frequently detected in chlorinated water supplies.

Several standards were used for these analyses. The "Purgeable A" standard was purchased from Supelco, Inc. (Catalog 13, Cat. No. 4-8815) and contained the following compounds at a concentration of 0.2 mg/mℓ in methanol:

Methylene chloride	Trichloroethylene
1,1-dichloroethylene	1,1,2-trichloroethylene
1,1-dichloroethane	Dibromochloromethane
Chloroform	Tetrachloroethylene
Carbon tetrachloride	Chlorobenzene
1,2-dichloropropane	

This base standard was added to boiled and purged water, to form a solution containing 10 µg/ℓ of each compound listed above.

Battelle-prepared standards were of two different concentrations and contained chloroform, carbon tetrachloride, and trichloroethylene. One standard was at the 3 µg/ℓ level, and the other at 8 µg/ℓ. The Battelle standards gave essentially the same detector response as the purchased standard and served as a cross-check on the validity of the method. A summary of the results of the analyses of the standards is given in Table 6.

The reproducibility of the method based on the Battelle standards was approximately 10 percent relative. The Battelle standards compared to the Supelco A standard indicated that an error as high as 41 percent might exist for the Supelco A standard for carbon tetrachloride. Blank water used to make the standards was also sparged and no interferences detected. This three-point cross-check to verify the validity of the purchased standard, which was used in this work, shows an agreement for the three components of 5 to 40 percent.

Base Neutral Extractables and Phenolic Compounds--

The initial attempt to determine the non-volatile organics was made in July, 1978. However, the results obtained then were discarded because of

TABLE 6. VOLATILE HALOGENATED HYDROCARBONS[a]
(Reported as Micrograms/Liter)

Compounds	Sample designation 001[b]	002[c]	003[d]	004-5[e]	006-7[f]	008-9[g]
Chloroform	1.2	1.2	1.0	0.8	0.6	1.2
1,1-dichloroethane	0.4	<0.01	0.9	0.6	0.01	0.7
1,1,1-trichloroethane (methyl chloroform)	1.9	2.1	1.6	2.0	2.0	1.3
Carbon tetrachloride	2.3	1.9	1.7	1.5	1.7	1.5
1,2-dichloropropane	1.3	1.8	0.6	1.2	1.3	0.6
1,3-dichloropropene	0.2	<0.01	0.6	0.2	<0.01	0.4
Trichloroethylene	0.8	0.9	0.8	0.7	0.7	0.4
Trichloroethane	0.9	1.4	0.5	0.7	1.1	0.1
Tetrachloroethylene or tetrachloroethane	<0.01	<0.01	0.05	0.02	--[h]	0.05

(a) Analyses were completed on July 8, 1978

(b) Plant effluent 6/21/78

(c) Wood tank influent 6/21/78

(d) Lagoon influent 6/21/78

(e) Plant effluent 6/22/78

(f) Wood tank influent 6/22/78

(g) Lagoon influent 6/22/78

(h) Chromatograph stopped before reaching this compound.

TABLE 7. SUMMARY OF THE RESULTS FROM THE ANALYSES OF STANDARD SAMPLES

	Chloroform	Carbon tetrachloride	Trichloro-ethylene
Battelle std. #1			
Concentration, µg/l	2.81	3.19	6.19
Integrator counts per µg/l	23,181	90,958	78,595
Battelle std. #2			
Concentration, µg/l	7.03	7.98	7.98
Integrator counts per µg/l	29,182	72,671	83,750
Counts average	26,182	81,815	81,143
Supelco std. A			
Concentration, µg/l	10.0	10.0	10.0
Integrator counts per µg/l	27,604	58,190	123,680
% deviation from Battelle stds.	5.2	40.6	34.5

TABLE 8. RESULTS OF THE BASE NEUTRAL EXTRACTABLES AND PHENOLICS ANALYSES
(Analyses completed on December 16, 1978)

Compound	Amount found in sample, µg/ℓ								
	001	002	003	004-005	005	006-007	007	008-009 Phenols	008-009 Comp.
Bis - (2 chloroethyl) ether	a	a	a	a	a	a	a	a	a
1,3 - dichlorobenzene	a	a	a	a	a	a	a	a	a
1,4 - dichlorobenzene	a	a	a	a	a	a	a	a	a
1,2 - dichlorobenzene	a	a	a	a	a	a	a	a	a
Bis - (2 chloroisopropyl) ether	a	a	a	a	a	a	a	a	a
N-nitrosodipropylamine	a	a	a	a	a	a	a	a	a
Hexachloroethane	a	a	a	a	a	a	a	a	a
Nitrobenzene	a	a	a	a	a	a	a	a	a
Isophorone	a	a	a	a	a	a	a	a	a
Bis (2-chloroethoxy) methane	a	a	a	a	a	a	a	a	a
1,2,4 - trichlorobenzene	a	a	a	a	a	a	a	a	a
Naphthalene	0.5	0.7	1.7	1.5	0.6	0.3	0.9	10.1	2.3
Hexachlorobutadiene	a	a	a	a	a	a	a	a	a
Hexachlorocyclopentadiene	a	a	a	a	a	a	a	a	a
2-chloronaphthalene	a	a	a	a	a	a	a	a	a
2,6-dinitrotoluene	a	a	a	a	a	a	a	a	a
Dimethyl phthalate	<0.1	<0.1	a	<0.1	0.1	0.1	0.1	a	a
Acenaphthylene	a	a	a	a	a	a	a	a	a
Acenaphthene	1.7	a	a	a	1.0	<0.1	a	a	a
2,4-dinitrotoluene	a	a	a	a	a	a	a	a	a
Diethylphthalate	0.2	0.2	2.6	0.1	0.1	0.1	a	a	a
Fluorene	a	a	a	0.4	a	a	a	a	a
4-chlorophenyl phenyl ether	a	a	a	a	a	a	a	a	a
N-nitrosodiphenylamine	a	a	a	a	a	a	a	a	a
4-bromophenyl phenyl ether	a	a	a	a	a	a	a	a	a
Hexachlorobenzene	a	a	a	a	a	a	a	a	a

(Continued)

TABLE 8. (Continued)

Compound	Amount found in sample, µg/ℓ 001	002	003	004-005	005	006-007	007	008-009 Phenols	008-009 Comp.	
Phenanthrene	0.1	<0.1	0.6	0.1	a	a	a	1.0	a	
Anthracene	a	a	a	a	a	a	a	a	a	
Di-n-butyl phthalate	2.4	1.2	1.6	0.2	0.5	2.6	3.5	a	a	
Fluoranthene	2.9	a	42.	5.4	0.1	a	a	120.	155.	
Pyrene	a	a	a	a	a	a	a	a	a	
Butyl benzyl phthalate	0.1	0.2	a	0.4	0.3	1.2	3.4	a	a	
Chrysene	a	a	a	a	a	a	a	a	a	
Benzo (a) anthracene	a	a	a	a	a	a	a	a	a	
Bis - (2 ethylhexyl) phthalate	0.1	0.8	0.7	a	0.4	1.3	3.3	0.8	4.3	
Di-n-octyl phthalate	a	a	a	a	a	a	a	a	a	
Benzo (b) fluoranthene	a	a	a	a	a	a	a	a	a	
Benzo (k) fluoranthene	a	a	a	a	a	a	a	a	a	
Benzo (a) pyrene	a	a	a	a	a	a	a	a	a	
Benzo (g,h,i) perylene	a	a	a	a	a	a	a	a	a	
Indeno (1,2,3-cd) pyrene	a	a	a	a	a	a	a	a	a	
Dibenzo (a,h) anthracene	a	a	a	a	a	a	a	a	a	Neutrals
Phenol	2.4	1.6	11.6	1.7	1.3	1.6	a	a	1.9	Phenols
2-chlorophenol	a	a	a	a	a	a	a	a	a	
2,4-dimethylphenol	a	a	a	a	a	a	a	a	a	
2,4-dichlorophenol	a	a	a	a	a	a	a	a	a	
2,4,6-trichlorophenol	a	a	a	a	a	a	a	a	a	
2-nitrophenol	a	a	a	a	a	a	a	a	a	
4-chloro-3-methyl phenol	a	a	a	a	a	a	a	a	a	
4-nitrophenol	a	a	a	a	a	a	a	a	a	
4,6-dinitro-o-cresol	a	a	a	a	a	a	a	a	a	
Pentachlorophenol	a	a	a	a	a	a	a	a	<0.1	
2,4-dinitrophenol	a	a	a	a	a	a	a	a	a	

(a) Not detected. Detection limit ~1 µg/ℓ.

difficulties encountered with a newly-installed GC/MS system. The analyses were repeated in December, 1978, and the results of the base neutral extractables are presented in Table 7. Of the 42 base neutral extractable compounds sought, only 10 were above the detection limits of the GC/MS procedure which was used in analyzing the influents to and effluents from the continuous treatment system: included in these 10 were 5 phthalates, naphthalene, acenaphthene, fluorene, phenanthrene, and fluoranthene. Of the 11 phenolics, only phenol was present in the samples analyzed except for a trace (<0.1 µg/ℓ) of pentachlorophenol in the composite treatment plant influent from the lagoon.

The quality control procedures which were used during analysis of the nine wastewater samples for the semivolatile priority pollutants were as follows:

- Two process blanks were extracted along with the wastewater samples. One blank consisted of distilled water and the other blank was received with the wastewater samples. These blanks were analyzed by GC/MS.

- The percentage recoveries for the semivolatile priority pollutants were determined by spiking two distilled water samples with the priority pollutant semivolatile compounds and then extracting them along with the wastewater samples. The spiked samples were also analyzed by GC/MS. The results of these recovery studies are shown in Table 8.

- Strict performance criteria were followed to ensure that the GC/MS/DS were providing the highest quality chromatograms and mass spectra possible as described previously.

Benzidines--

Nine influent and effluent samples from the continuous waste treatment system were analyzed for benzidines and dichlorobenzidines using high pressure liquid chromatography and an electrochemical detector. The results of these analyses are given in Table 9.

TABLE 8. PERCENT RECOVERY OF PRIORITY POLLUTANTS SPIKED IN WATER

Compound	Run 1	Run 2	Average
Neutrals			
Bis-(2-chloroethyl) ether	116	108	112
1,3-Dichlorobenzene	92	67	80
1,4-Dichlorobenzene	92	67	80
1,2-Dichlorobenzene	96	84	90
Bis-(2-chloroisopropyl) ether	124	112	118
N-Nitrosodipropylamine	120	91	106
Hexachloroethane	92	87	90
Nitrobenzene	132	119	126
Isophorone	(a)	(a)	(a)
Bis-(2-chloroethoxy) methane	112	87	100
1,2,4-Trichlorobenzene	100	88	94
Naphthalene	108	89	99
Hexachlorobutadiene	56	60	58
Hexachlorocyclopentadiene	(a)	(a)	(a)
2-Chloronaphthalene	108	73	91
2,6-Dinitrotoluene	116	94	105
Dimethyl phthalate	128	116	122
Acenaphthalene	84	59	72
Acenaphthene	80	67	74
2,4-Dinitrotoluene	100	72	86
Diethyl phthalate	56	53	55
Fluorene	80	65	73
4-Chlorophenyl phenyl ether	60	55	57
N-Nitrosodiphenylamine	112	91	102
4-Bromophenyl phenyl ether	116	81	99
Hexachlorobenzene	148	107	128
Phenanthrene	108	79	94
Anthracene	104	85	95
Di-n-butyl phthalate	140	163	152
Fluoranthene	88	42	65
Pyrene	80	40	60
Butylbenzyl phthalate	124	56	90
Chrysene	80	11	46
Benzo(a)anthracene	80	11	46
Bis(2-ethylhexyl) phthalate	116	48	82
Di-n-octyl phthalate	64	22	43
Benzo(b)fluoranthene	48	22	35
Benzo(k)fluoranthene	48	22	35

TABLE 8. (Continued)

Compound	Run 1	Run 2	Average
Benzo(a)pyrene	48	16	32
Benzo(g,h,i)perylene	24	11	18
Indeno(1,2,3-cd)pyrene	32	16	24
Dibenzo(a,h)anthracene	(b)	(b)	(b)
Phenol	136	108	122
2-Chlorophenol	90	67	79
2,4-Dimethylphenol	36	30	33
2,4-Dichlorophenol	20	24	22
2,4,6-Trichlorophenol	84	92	88
2-Nitrophenol	20	34	27
4-Chloro-3-methylphenol	76	90	83
4-Nitrophenol	48	44	46
4,6-Dinitro-o-cresol	150	150	150
Pentachlorophenol	78	94	86
2,4-Dinitrophenol	114	140	127

(a) Compound not contained in standard used to spike samples.

(b) Level of compound below detection limits.

TABLE 9. RESULTS OF BENZIDINE ANALYSES[a]

Sample no.	Sample site	Analytical results	
		Benzidine, µg/ℓ	Dichlorobenzidine, µg/ℓ
001	Treatment plant effluent (6/21/78) [b]	<1	<1
002	Influent from wood tank to treatment plant (6/21/78) [b]	<1	<1
003 (Phenol)	Influent from lagoon to treatment plant (6/21/78) [c]	<1	<1
004/005	Treatment plant effluent (6/22/78) [d]	<1	<1
005	Treatment plant effluent (6/22/78) [d]	<1	<1
006/007	Influent from wood tank to treatment plant (6/22/78) [d]	<1	<1
007	Influent from wood tank to treatment plant (6/22/78) [b]	<1	<1
008	Influent from lagoon to treatment plant (6/22/78) [b]	<1	<1
008/009 (Phenol)	Influent from lagoon to treatment plant (6/22/78) [c]	<1	<1

(a) Analyses were completed on December 16, 1978.

(b) Aliquots of composite samples prepared and preserved expecially for organic analyses.

(c) Grab samples preserved for phenol analyses.

(d) Grab samples preserved for organic analyses.

SECTION 5

DISCUSSIONS OF EFFECTIVENESS OF THE CONTINUOUS TREATMENT SYSTEM FOR THE REMOVAL OF PRIORITY POLLUTANTS

WASTE LOADS PER 24-HOUR PERIOD

The analytical results and the average daily flow rates measured for the sampling period were used to calculate the waste loads of the priority pollutants for the influent and the effluent waste streams related to the continuous treatment system.

Priority Pollutant Loads

The mass flow of the priority pollutants entering and leaving the wastewater treatment plant daily are given in Table 10. The compounds and elements whose concentrations were below detection limits were assumed to be absent and were not included in the loading calculations.

REMOVAL EFFICIENCIES

The efficiency for the removal of the priority pollutants by the technique of lime and settle (pH = 8.5) is also given in Table 10. The efficiency was calculated by the following method:

$$\frac{[(kg/day)_{inf} - (kg/day)_{eff}]}{(kg/day)_{inf}} \times 100 = \text{Removal efficiency, percent.}$$

Of the priority pollutants, 97 percent of the chromium was removed, or better. More than 88 percent of the zinc and fluoranthene was removed, and more than 78 percent of the base neutral organics was removed. Copper and cadmium removals were about 70 and 64 percent, respectively.

CONCLUSION

The technique used for the removal of metals at this airplane parts plant removes 97 percent of the chromium, 88 percent of the zinc, and about 70 percent of the copper. It also is effective for removing the base neutral organic compounds (>78 percent). Cyanide is almost completely removed in a batch pretreatment system. The volatile organic compounds are not removed to a detectable extent.

TABLE 10. WASTE LOAD OF PRIORITY POLLUTANTS IN A 24-HOUR PERIOD

	Influent kg/day	Effluent kg/day	Removal efficiency, %
Metals:			
Cadmium	0.055	0.02	63.6
Chromium	18.88	0.436	97.7
Copper	0.27	0.082	70.0
Nickel	0.055	0.055	--
Zinc	0.236	0.027	88.6
Volatile organics	0.016	0.016	--
Base neutral organics	0.065	0.014	78.5
Fluoranthene	0.06	0.007	88.3
Phenol	0.005	0.003	40.0

BIBLIOGRAPHY

(1) Sampling and Analysis Procedures for Screening Industrial Effluents for Priority Pollutants. Staff of the Environmental Monitoring and Support Laboratories, U.S. EPA, Cincinnati, Ohio, March, 1977 (rev. April, 1977).

APPENDIX A

SAMPLE LOG

Following is a list of samples collected at the facility June 21-22, 1978.

TABLE A-1. SAMPLE AND ANALYTICAL LOG

Sample no.	Location	Type	Date of collection
001	Plant effluent	3-gal composite	6-21-78
	"	grab-cyanide	"
	"	grab-phenol	"
	"	grab-oil & grease	"
	"	grab-organics	"
	"	distilled H_2O blank	"
002	Wood tank influent	3-gal composite	"
	(to treatment plant)	grab-cyanide	"
	"	grab-phenol	"
	"	grab-oil & grease	"
	"	grab-organics	"
	"	distilled H_2O blank	"
003	Lagoon influent	3-gal composite	"
	(to treatment plant)	grab-cyanide	"
	"	grab-phenol	"
	"	grab-oil & grease	"
	"	grab-organics	"
	"	distilled H_2O blank	"
004	Plant effluent	3-gal composite	6-22-78
005*	Plant effluent	3-gal composite	"
004-005	"	grab-cyanide	"
	"	grab-phenol	"
	"	grab-oil & grease	"
	"	grab-organics	"
006	Wood tank influent (to treatment plant)	3-gal composite	"
007*	Wood tank influent (to treatment plant)	3-gal composite	"
006-007	"	grab-cyanide	"
	"	grab-phenol	"
	"	grab-oil & grease**	"
	"	grab-organics	"

(continued)

TABLE A-1. (Continued)

Sample no.	Location	Type	Date of collection
008	Lagoon influent (to treatment plant)	3-gal composite	6-22-78
009*	Lagoon influent (to treatment plant)	3-gal composite	"
008-009	"	grab-cyanide	"
	"	grab-phenols	"
	"	grab-oil & grease	"
	"	grab-organics	"
010	Oil system influent	grab-cyanide	6-21-78
011	"	grab-organics	"
012	"	grab-oil & grease	"
013	"	grab-phenols	"
	"	distilled H_2O blank	"
014	Zyglo influent	grab-cyanide	"
015	"	grab-phenol	"
016	"	grab-metals	"
017	"	grab-organics	"
018	"	grab-oil & grease	"
019	"	distilled H_2O blank	"
020	Oil system treated	grab-cyanide	"
021	"	grab-organics	"
022	"	grab-oil & grease	"
023	"	grab-phenols	"
024	"	grab-metals	"
025	"	distilled H_2O blank	"
026	Chrome tank influent	grab-metals	"
030	Cyanide input	grab-metals	6-22-78
031	"	grab-phenols	"
032	"	grab-cyanide	"
033	"	grab-oil & grease	"
034	"	grab-organics	"
035	Cyanide output	grab-metals	"
036	"	grab-phenols	"
037	"	grab-cyanide	"
038	"	grab-oil & grease	"
039	"	grab-organics	"
046	Cyanide - after Cl_2	grab-cyanide	"
047**	Cyanide - after Cl_2	grab-metals	"
048	Boeing source water	2-gal grab	"
049	Zyglo	grab-oil & grease	"
050	"	grab-cyanide	"
051	"	grab-phenols	"
052	"	grab-metals	"
053	"	grab-organics	"

* Duplicate sample
** Broken in shipping

APPENDIX B

SUMMARY OF ANALYTICAL PROCEDURES FOR THE PRIORITY ORGANIC POLLUTANTS

The general scheme used for the analysis of the organic constituents of the wastewater samples is given in Figure 2. Volatile components are determined by a purge-and-trap technique. Semivolatile components are initially extracted with dichloromethane under acidic conditions. Acidic conditions yield better recovery efficiencies and fewer emulsion problems than alkaline conditions. The acidic components in the initial extracts are separated from the neutral components by extraction into 0.2 N NaOH.

Benzidines are separated from neutral and acidic compounds present in a separate chloroform extract of a neutral water sample by extracting the chloroform with 2 N H_2SO_4. The exceptionally strong acidic conditions are necessary for the extraction of 3,3'-dichlorobenzidine. Ethanol or methanol must be present during the solvent concentration steps to avoid decomposition of the benzidine.

The benzidines are quantified by high pressure liquid chromatography (HPLC) using an electrochemical detector which is a highly sensitive and selective system. All other separation, identification, and quantification is achieved by combined gas chromatography-mass spectrometry-data system using high resolution glass capillary columns. Some of the details of the analytical procedure are given below.

EXTRACTION PROCEDURE

Half-gallon jugs containing 1,500 mℓ of water sample, 5 g of $KHSO_4$, and 75 g of NaCl are treated with 150 mℓ of dichloromethane and 1 mℓ of concentrated H_2SO_4. The mixture is then stirred in the jug with a magnetic stirrer for 2 hours. The rate of stirring is such that a slight vortex is formed at the water-dichloromethane interface but not fast enough to form emulsions. After the solution is stirred for 2 hours, the dichloromethane layer is transferred with a 50-mℓ syringe to a 500-mℓ separatory funnel with a Teflon stopcock. The aqueous solution is re-extracted two times with 50 mℓ of dichloromethane for 30 minutes and the dichloromethane layers are combined with the first extract (about 210 mℓ of dichloromethane is recovered).

The combined dichloromethane extract, containing the acidic and neutral compounds, is extracted twice with 200-mℓ aliquots of 0.2 N NaOH with vigorous shaking for 2 minutes and washed with 0.1 N HCl. The resulting dichloromethane, containing only the neutrals, is dried with ~5 g $MgSO_4$ and concentrated to

1 mℓ using a Kuderna-Danish apparatus. Then 1 mℓ of benzene and a solution containing 20 µg of hexaethylbenzene (HEB) as an internal standard are added and the solution is concentrated to 0.4 mℓ for GC and GC/MS analysis.

The 0.2 N NaOH extracts containing the sodium salts of acid compounds are combined in a 500-mℓ separatory funnel, acidified with 20 mℓ of 6 N HCl (pH 1.0-1.5) and extracted three times with 50 mℓ of dichloromethane. The combined dichloromethane layers are dried over $MgSO_4$ and concentrated to 1 mℓ. This extract, containing the acids, is methylated with diazomethane. Then 1 mℓ of benzene and a solution containing 20 µg of the internal standard, hexaethylbenzene (HEB), are added and the solution is concentrated to 0.4 mℓ for GC and GC/MS analysis.

GC/MS ANALYSIS

Capillary Column GC/MS Instrumentation

The GC/MS/DS used is a Finnigan Model 9500 gas chromatograph directly interfaced to a Finnigan Model 3200 quadrupole mass spectrometer. Data acquisition and manipulation are controlled by a Systems Industries Model 150 data system. The column used for all the analyses is a 30 m x 0.2 mm I.D. glass capillary coated with SE-30 and supplied by J & W Scientific. Samples (2.0 µℓ) are injected through a Grob injector operated in the splitless mode. Following injection the column is held for 5 minutes at 60°C, then temperature programmed at 4°/min. to 270°C and held at 270°C for 15 minutes. The computer retention time clock is started during injection. Data acquisition is started at the end of about six minutes. The sensitivity of the MS is generally 10^{-8} amp/volt at an electron multiplier setting of 1800 volts.

Strict performance criteria are followed to ensure that the GC/MS/DS is providing the highest quality chromatograms and mass spectra possible. Prior to each day's GC/MS data acquisition, a test mixture is analyzed to test the complete GC/MS system for the following characteristics:

- MS tune-up
- Splitless injection system
- Capillary column efficiency
- Capillary column acidity or basicity
- Presence of adsorptive sites on the column
- Detection limit
- GC/MS transfer line losses.

The compounds in the test mixture include:

1-naphthylamine	Tridecylbenzene
2-methylnaphthol	n-eicosane
1-pentadecanol	Pyrene
Decafluoretriphenylphosphine	n-heneicosane
3-methylnonadecane	Methyl stearate
2-methyleicosane	

Computerized Compound Search Routine

The computerized compound search is used on all the semivolatile extractable pollutant standard solutions and wastewater extracts.

The first step in using the computer to search for specific compounds is to enter the compounds and search parameters into a queue editor computer program. The search program parameters are chosen to minimize false negative responses at the expense of the possible production of false positives. The GC/MS data for each of the priority pollutants is listed in Table B-1. It must be emphasized that the mass spectrum of each "hit" is manually examined before the presence of a specific compound is reported. The search parameters are determined by analyzing standard solutions containing all the priority pollutants of concern and hexaethylbenzene (HEB) internal standard. The mass spectrum of each of the compounds in the standard mixture is identified by comparison to published spectra and the retention time of each of the compounds is recorded. Separate samples are analyzed containing the neutrals and methylated phenols. The search parameters for each of these groups of compounds are entered into a separate editor program. The search parameters include the compound name, the retention time, and two or three chemically significant fragment masses. In order to enhance search selectivity, a threshold may be assigned. The threshold value directs the search program to sum the set of ions only if each ion intensity is equal to or greater than the specified percentage of the highest intensity. The value one was used for all the searches for this study. One of the masses in the search program may also be selected as the base peak (most intense ion) which directs the search program to perform the summation only if the indicated mass exhibits the largest intensity of the selected ions.

Following GC/MS analysis of a sample, the data file is transferred to the search disc containing the search parameters and the search program. Once the program is initiated, the user enters the spectrum data file name and the queue editor file name containing the search data for the compounds of interest. The program then requests from the user the retention time of the internal standard. If a value is entered, the program searches on the basis of relative retention time; if no value is entered, the search proceeds on the basis of retention time. The program then requests a search window (e.g., 300 scans) to be used for each specific compound search.

Four different output modes are available with the program. For this study the output consisted of a CRT image of the reconstructed gas chromatogram (RGC) of the search window on the lower half of the screen and the selected ion summation mass chromatogram of the compound searched for on the top half of the screen. Following the appearance of the RGC and SIS (Selected Ion Summation) plot on the screen a hardcopy list of the results is printed. If the user has selected the CRT graphic option, the program allows a pause for the RGC and SIS plot to appear on the screen until the RETURN key is pressed. When the pause occurs during the search the user is provided with several options such as horizontal expansion, vertical amplication, area determination for quantification as described in the next section, and also queuing of the spectrum for later printout. If areas are determined, these data are included in the hardcopy list.

TABLE B-1. GC/MS DATA USED FOR DETERMINING SEMIVOLATILE PRIORITY POLLUTANTS

Compound	Approx. retention index(a)	Approx. retention time, min.(b)	M.W.	Ions used for quantification, m/e (intensity)
		Neutrals		
Bis-(2-chloroethyl) ether	975	10.5	142	93(100), 63(99), 95(31)
1,3-dichlorobenzene	994	10.6	146	146(100), 148(65), 111(35)
1,4-dichlorobenzene	999	10.6	146	146(100), 148(65), 111(35)
1,2-dichlorobenzene	1017	11.2	146	146(100), 148(65), 111(35)
Bis-(2-chloroisopropyl) ether	1025	11.7	170	45(100), 77(19), 79(12)
N-nitrosodipropylamine	1035	12.6	130	70(100), 130(30)
Hexachloroethane	1050	13.0	234	201(100), 117(90)
Nitrobenzene	1065	13.4	123	77(100), 123(50)
Isophorone	1100	14.6	138	82(100), 138(15)
Bis-(2-chloroethoxy)methane	1125	15.5	180	93(100), 95(32), 123(21)
1,2,4-trichlorobenzene	1150	16.8	180	180(100), 182(97)
Naphthalene	1158	17.1	128	128(100), 127(15)
Hexachlorobutadiene	1200	18.8	258	225(100), 227(60)
Hexachlorocyclopentadiene	1315	22.7	270	237(100), 235(63), 272(12)
2-chloronaphthalene	1330	24.0	162	162(100), 127(40)
2,6-dinitrotoluene	1370	25.5	150	165(100), 89(80)
Dimethyl phthalate	1415	26.3	194	163(100), 77(21)
Acenaphthalene	1420	27.0	152	152(100), 151(23)
Acenaphthene	1445	27.2	154	153(100), 154(90)
2,4-dinitrotoluene	1475	27.9	150	165(100), 63(60)
Diethyl phthalate	1550	30.4	222	149(100), 178(25)
Fluorene	1555	30.5	166	166(100), 165(90)
4-chlorophenyl phenyl ether	1570	30.6	204	204(100), 141(75)
N-nitrosodiphenylamine(c)	1590	31.4	198	169(100), 168(72)
4-bromophenyl phenyl ether	1650	33.0	248	248(100), 250(95)
Hexachlorobenzene	1675	33.4	282	282(100), 284(77)
Phenanthrene	1740	35.6	178	178(100), 176(17)
Anthracene	1750	35.9	178	178(100), 176(17)
Di-n-butyl phthalate	1920	40.1	278	149(100), 104(10)
Fluoranthene	2020	42.5	202	202(100), 101(25)
Pyrene	2060	43.7	202	202(100), 101(25)

(Continued)

TABLE B-1. CONTINUED

Compound	Approx. retention index[a]	Approx. retention time, min[b]	M.W.	Ions used for quantification, m/e (intensity)
Butylbenzyl phthalate	2300	48.5	298	149(100), 91(62)
Chrysene	2395	50.9	228	228(100), 226(27)
Benzo(a)anthracene	2405	51.2	228	228(100),
Bis(2-ethylhexyl) phthalate	2515	52.9	390	149(100), 167(38)
Di-n-octyl phthalate	2720	55.9	390	149(100), 167(34)
Benzo(b)fluoranthene	2704	56.4	252	252(100), 253(23)
Benzo(k)fluoranthene	2750	56.9	252	252(100), 253(23)
Benzo(a)pyrene	3000	62.8	252	252(100), 253(23)
Benzo(g,h,i)perylene	3059	66.8	276	276(100)
Indeno(1,2,3-cd)pyrene	3180	68.3	276	276(100)
Dibenzo(a,h)anthracene	3330	72.5	278	278(100)
		Phenols		
2-chlorophenol(free)	970	11.0	128	128(100), 130(33)
Phenol	1059	11.7	94	94(100), 66(60), 65(35)
2-chlorophenol(Me)	1095	15.1	142	142(100), 99(85), 127(54), 144(30)
2,4-dimethylphenol	1175	16.9	122	107(100), 121(97), 122(85)
2,4-dichlorophenol	1240	18.1	162	162(100), 164(66)
2,4-dichlorophenol(Me)	1279	21.0	176	161(100), 133(88), 163(65)
2,4,6-trichlorophenol(Me)	1301	22.6	210	195(100), 197(95), 167(75)
2-nitrophenol(Me)	1325	22.9	143	77(100), 106(80), 92(65)
4-chloro-3-methylphenol(free)	1330	23.3	156	107(100), 142(69), 77(62)
4-nitrophenol(Me)	1347	24.8	143	107(100), 77(82), 153(12)
4,6-dintro-o-cresol(Me)	1637	33.8	196	89(100), 165(61), 182(58), 65(61), 53(55)
Pentachlorophenol(Me)	1687	34.9	278	237(100), 265(91), 280(70)
2,4-dinitrophenol(Me)	1742	35.5	198	76(100), 151(69), 168(62)
		Internal Standard		
Hexaethylbenzene	1680	34.0	246	231(100), 246(30)

(a) Retention indices vary slightly depending upon the polarity of the column.
(b) GC Conditions: 30m x 0.26mm ID glass Capillary column coated with SE-30. Column was held at 60°C for 5 minutes then programmed at 4 degrees per minute to 270°C and held at 270°C for 15 minutes.
(c) Decomposes upon injection in the GC to diphenylamine; therefore it is detected as diphenylamine.

Occasionally several peaks may appear on the SIS output above the RGC, any one of which could be the searched compound. However, the peak should occur near the center of the search window. The user can then move the vertical cursor to select a spectrum and a background for entry into a Queue file. At the end of the search the spectra can then all be printed out automatically for manual inspection to determine if the searched compound was actually present.

Quantification

The method for quantification of the priority pollutants in the wastewater extracts is based on the GC/MS analysis using area counts under the extracted ion current profiles (EICP) from the SIS portion of the computer program. The ions used for quantification are the same ions used to search for the compound in the search routine. The area reported is independent of the amplification of the trace, allowing the user to amplify low intensity chromatographic peaks for the purpose of properly delimiting the peak. Although the dual display format individually normalizes the selected ion and total ion traces, the program maintains internally their true relationship used for area determinations. Areas may be determined either by tangential "skimming" of a smaller peak on the tail of a larger one or by a perpendicular drop to the x-axis of the display simply by proper positioning of the crosshairs.

Quantification of wastewater samples is based on the area counts of the compound compared to the area counts of the hexaethylbenzene (HEB) internal standard. However, the mass spectrometric response is somewhat different for each compound because of differing degrees of fragmentation and ionization efficiencies. Therefore, standard solutions were analyzed containing all extractable priority pollutants at three different concentrations, but each containing 50 ng/μℓ of HEB. This same quantity of HEB is then added to each of the wastewater extracts just prior to GC/MS analysis. For each of the standard solutions, the area counts of the priority pollutant are divided by the area counts of the internal standard. This value is then multiplied by a factor to bring the concentration of the priority pollutant equal to that of the internal standard. For example, when the concentration of the priority pollutant is 10 ng/μℓ and the concentration of the internal standard is 50 ng/μℓ, the value is multiplied by 5. This number represents the relative mass spectrometric response factor between the two compounds. For quantification of the priority pollutants in the wastewater extracts, an adjusted response factor was used based on the results of the three standards.

The amount of priority pollutant in each extract is calculated using the following equation:

$$\text{ppb} = \frac{\mu g}{\ell} = \frac{\text{Area Counts Compound}}{\text{Area Counts HEB}} \times \frac{\text{Amount HEB } (\mu g) \times \text{MS Response Factor}}{\text{Amount of Water } (\ell)}$$

The early-eluting compounds did not yield quite as precise peak area ratios as the later-eluting compounds due to the relatively small number of scans across the peak (e.g., 3 or 4 scans) and also because of some tailing for a few of the more polar compounds. From the results of the GC/MS analyses of the priority pollutant standards, we estimate that the maximum relative error is $\pm$ 50 percent, although the results should be somewhat better for the later eluting compounds.